C 126/2/987

Preprint from the 1987

BUREAU OF MINES MINERALS YEARBOOK

Calcium and Calcium Compounds

UNITED STATES DEPARTMENT OF THE INTERIOR

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This publication is a chapter from the current Bureau of Mines Minerals Yearbook, comprising *Volume I, Metals and Minerals; Volume II, Area Reports: Domestic; Volume III, Area Reports: International.* The separate volumes of the Yearbook are sold by the Superintendent of Documents, Washington, D.C. 20402.

Calcium and Calcium Compounds

By David E. Morse[1]

Calcium, the fifth most abundant element in the earth's crust, is chemically very active and is found in nature in a host of minerals that occur in nearly every geologic environment. The Bureau of Mines publishes reports for a variety of calcium-containing minerals and compounds because of their commercial significance and contribution to the quality of human life. The commercial name for calcium fluoride is fluorspar; calcium carbonate is sold as either limestone, marble, calcareous marl or shell; calcium sulfate is gypsum or anhydrite; calcium oxide and hydroxide are called lime; and calcium phosphate (apatite) is known as phosphate rock. Information on these products can be obtained in the chapters of the Bureau of Mines Minerals Yearbook entitled "Fluorspar," "Gypsum," "Lime," "Phosphate Rock," "Crushed Stone," and "Dimension Stone." Other calcium compounds are discussed in the chapter concerning the element with which calcium is combined; for example, calcium bromide is covered in the "Bromine" chapter. This chapter includes calcium metal, calcium chloride, and various other calcium compounds not covered elsewhere.

Calcium metal was manufactured by one company in Connecticut. Natural calcium chloride was produced by three companies in California, two companies in Michigan, and one company in Washington. Synthetic calcium chloride was manufactured by two companies in Louisiana and one company in Washington.

Domestic Data Coverage.—Domestic production data for calcium chloride are developed by the Bureau of Mines from a voluntary survey of U.S. operations entitled "Calcium Chloride and Calcium-Magnesium Chloride." Of the 10 operations to which a survey request was sent, 9 responded, representing less than one-half of the total production shown in table 1. Production for the single nonrespondent, Dow Chemical Co. at Ludington, MI, was estimated using published plant capacity and information reported in trade journals and research reports.

DOMESTIC PRODUCTION

Pfizer Inc. produced calcium metal at Canaan, CT, by the Pidgeon process, an aluminothermic process in which high-purity calcium oxide (produced by calcining limestone) and aluminum powder are briquetted and heated in vacuum retorts. The vaporized calcium metal product is collected as a crown in a water-cooled condenser.

Pfizer produced commercial-grade calcium containing 98.5% calcium in seven shapes, high-purity redistilled metal containing 99.2% calcium in four shapes, and an 80% calcium-20% magnesium alloy. Pfizer also produced an alloy consisting of 75% calcium and 25% aluminum for use in maintenance-free batteries, and a pure calcium wire used in the steel industry to modify inclusions. Elkem Metals Co., a Norwegian-owned company with headquarters at Pittsburgh, PA, produced calcium alloys at its plant in Alloy, WV, including a calcium-silicon alloy containing about 30% calcium, 65% silicon, and 5% iron, and two proprietary alloys that contain barium, and

barium and aluminum. The Foote Mineral Co., ASARCO Incorporated, and The Pesses Co. also produced calcium alloys.

National Chloride Co. of America, Cargill Inc.'s Leslie Salt Co., and Hill Bros. Chemical Co. produced calcium chloride from dry-lake brine wells in San Bernardino County, CA. Hill Bros. Chemical also produced from a second operation near Cadiz Lake. Natural calcium chloride production in California was much less than the quantity produced in Michigan. Dow and Wilkinson Chemical Corp. recovered calcium chloride from brines in Lapeer and Mason Counties, MI. Dow's Ludington plant produced calcium chloride pellets and flake; Wilkinson marketed calcium chloride solutions only. Tahoma Chemical Co. Inc. produced natural calcium chloride in Washington.

Allied Signal Inc. recovered synthetic calcium chloride as a byproduct at its Baton Rouge, LA, plant using hydrochloric acid and limestone; Texas United Chemical Corp. produced calcium chloride from purchased hydrochloric acid and limestone at its plant near Lake Charles, LA; and Occidental Chemical Corp. manufactured calcium chloride at Tacoma, WA, using limestone and hydrochloric acid.

Texas United Chemical produced granular calcium chloride at Lake Charles, LA. Total capacity was reported to be 40,000 short tons per year of liquid and dry calcium chloride, 100% basis.

Calcium hypochlorite was produced by Olin Corp. and PPG Industries Inc. Total domestic calcium hypochlorite capacity was 165,000 tons per year.

Table 1.—U.S. production of calcium chloride (75% $CaCl_2$ equivalent)

Year	Natural		Synthetic		Total	
	Quantity (short tons)	Value (thousands)	Quantity (short tons)	Value (thousands)	Quantity (short tons)	Value (thousands)
1983	663,949	$71,330	192,688	$29,727	856,637	$101,057
1984[e]	838,000	93,000	198,000	31,500	1,036,000	124,500
1985	W	W	W	W	940,000	135,200
1986	W	W	W	W	780,000	[r]109,294
1987[e]	W	W	W	W	772,776	87,353

[e]Estimated. [r]Revised. W Withheld to avoid disclosing company proprietary data.

CONSUMPTION AND USES

Calcium metal was used in the manufacture of batteries, as an aid in removing bismuth in lead refining, as a desulfurizer and deoxidizer in steel refining, and as a reducing agent to recover refractory metals such as chromium, rare earths, and thorium from their oxides. Some minor uses were in the preparation of vitamin B and chelated calcium supplements and as a cathode coating in some types of photoelectric tubes. The nuclear applications of calcium metal give it strategic significance; foreign sales must be approved by the U.S. Department of State. State Department approval had been denied to countries that were not signatory to the United Nations Nuclear Nonproliferation Treaty. Calcium metal is used to reduce uranium dioxide, a fuel element utilized in some types of fission reactors.

Calcium chloride was used for road and pavement deicing, dust control and road base stabilization, coal and other bulk material thawing, oil and gas drilling, concrete-set acceleration, tire ballasting, and miscellaneous uses.

The principal use of calcium chloride was to melt snow and ice from roads. Calcium chloride is more effective at lower temperatures than rock salt and has been used mainly in the Northern and Eastern States. Because of its considerably higher price, it was used in conjunction with rock salt for maximum effectiveness and economy.

Calcium hypochlorite was used to disinfect swimming pools, which accounted for 85% of domestic demand, and in other municipal and industrial bleaching and sanitation processes. It was used as an algicide, bactericide, deodorant, water purifier, disinfectant, fungicide, and bleaching agent.

Calcium nitrate was used as a concrete additive to inhibit corrosion of steel reinforcement bars, accelerate setting time, and enhance strength.

Calcium carbide and calcium-silicon alloy were used to remove sulfur from molten pig iron as it was carried in transfer ladles from the blast furnace to the steelmaking furnace.

Precipitated calcium carbonate was used as a pigment for brightness and opaqueness in premium-quality coated and uncoated papers.

PRICES AND SPECIFICATIONS

The published price of calcium metal crowns in quantities greater than 20,000 pounds was unchanged from that established November 1, 1985. The published price of calcium-silicon alloy remained unchanged. Yearend published prices and specifications were as follows:

	Value per pound	
	1986	1987
Calcium metal, 1-ton lots, 50-pound full crowns, 10 by 18 inches, Ca + Mg 99.5%, Mg 0.7%	$3.92	$3.92
Calcium-silicon alloy, 32% calcium carload lots, f.o.b. shipping point	.72	.72

Source: Metals Week. V. 57, No. 52, 1986, p. 5; v. 58, No. 52, 1987, p. 5.

Calcium metal was usually sold in the form of crowns, broken crown pieces or nodules, or billets, which are produced by melting crowns in an argon atmosphere. The metal purity in these forms was at least 98%. Higher purity metal was obtained by redistillation.

Calcium metal was usually shipped in polyethylene bags under argon in airtight 55-gallon steel drums.

Calcium chloride was sold as flake or pellet averaging about 75% $CaCl_2$, or as a liquid concentrate averaging 40% $CaCl_2$. Yearend 1987 published prices and specifications were as follows:

	Value per ton
Calcium chloride concentrate, regular grade, 77% to 80%, flake, bulk, carload, works	$153.00
100-pound bags, carload, same basis	196.00
Anhydrous, 94% to 97%, flake or pellet, bulk, carload, same basis	217.00
80-pound bags, carload, same basis	279.00
Brining grade, 80-pound bags	285.00
Calcium chloride liquid, 100% basis, tank car, tank truck, barge	99.75
45%, same basis	118.00
Calcium chloride, United States Pharmacopeia, granular, 225-pound drums, truckload, freight equalized	1,800.00

Source: Chemical Marketing Reporter. Dec. 28, 1987, p. 29.

FOREIGN TRADE

U.S. exports of calcium chloride increased significantly in quantity; exports to Canada were more than double those of 1986. Calcium hypochlorite was exported in small quantities to 76 countries worldwide for an export value of $28 million, or an increase of $5 million compared with that of 1986. Exports of calcium phosphates, which is used as a feed additive for livestock, were valued at $53.5 million and went to over 50 countries, primarily in the Western Hemisphere. The combined customs value for exported calcium borate, calcium carbide, calcium chloride, and other calcium compounds totaled $19.3 million.

Imports for consumption of calcium metal were from four countries—Canada, China, France, and the U.S.S.R. China supplied more than one-half of the quantity imported; France, about 23%; Canada, 15%; and the U.S.S.R., about 9%. Imports of crude calcium chloride showed a marked increase compared with those of 1986. Imports from Canada were responsible for most of the increase; Canada supplied over three quarters of U.S. imports. Allied increased operating rates at its Amherstburg, Ontario, Canada, facility after the shutdown of its synthetic, Solvay soda ash plant near Syracuse, NY, in 1986. Imports of a variety of calcium compounds are listed in tabular form in this report for the first time.

Table 2.—U.S. exports of calcium chloride, by country

Country	1986		1987	
	Short tons	Value[1]	Short tons	Value[1]
Canada	13,341	$2,308,561	28,718	$4,007,252
Mexico	448	132,904	704	231,133
Netherlands	595	132,530	471	636,332
Sweden	907	412,852	524	216,624
Switzerland	277	141,178	857	r79,966
United Arab Emirates	840	230,666	330	50,226
Venezuela	249	118,386	1,159	400,180
Other	r1,511	r485,170	1,955	885,566
Total	18,168	3,962,247	34,718	6,657,299

rRevised.
[1]U.S. Customs declared value.

Source: Bureau of the Census.

Table 3.—U.S. imports for consumption of calcium and calcium chloride

Year	Calcium		Crude calcium chloride		Other calcium chloride	
	Pounds	Value[1]	Short tons	Value[1]	Short tons	Value[1]
1983	332,834	$866,409	13,580	$654,490	204	$662,526
1984	248,973	669,586	21,803	1,341,166	275	475,749
1985	492,244	1,395,198	75,381	9,059,352	2,355	1,907,976
1986	566,170	1,310,084	143,328	14,403,393	2,098	1,263,552
1987	776,225	1,918,099	229,964	20,916,867	1,282	706,370

[1]U.S. Customs, insurance, freight.

Source: Bureau of the Census.

Table 4.—U.S. imports for consumption of calcium chloride, by country

Country	1986		1987	
	Short tons	Value[1]	Short tons	Value[1]
Crude:				
Canada	111,991	$9,317,161	180,786	$13,533,501
Germany, Federal Republic of	5,175	861,372	18,957	2,234,625
Mexico	516	12,614	5,422	952,860
Sweden	4,734	806,112	11,219	1,479,925
Other	20,912	3,406,134	13,580	2,715,916
Total	143,328	14,403,393	229,964	20,916,867
Other:				
Canada	363	418,256	489	433,831
Germany, Federal Republic of	1,286	460,180	54	83,699
Sweden	22	22,006	2	2,927
Other	427	363,110	737	185,913
Total	2,098	1,263,552	1,282	706,370

[1]U.S. Customs, insurance, freight.

Source: Bureau of the Census.

Table 5.—U.S. imports of other calcium chloride

	1986		1987	
	Short tons	Value[1]	Short tons	Value[1]
Calcium borate (crude)	39,158	$8,783,616	19,149	$3,326,187
Calcium bromide	3,109	965,988	4,038	1,016,511
Calcium carbide	17,616	5,645,762	15,881	5,502,804
Calcium carbonate, precipitated	18,706	7,832,341	16,001	7,883,693
Calcium carbonate, chalk whiting	5,457	1,160,048	5,319	1,174,752
Calcium carbonate (crude), natural chalk	154	2,085,85[illegible]	114	1,596,521
Calcium cyanamide	3,397	922,703	2,422	1,172,710
Calcium hypochlorite	7,034	10,167,855	8,192	11,811,590
Calcium nitrate	73	16,959,886	76	16,505,195
Dicalcium phosphate	1,566	1,347,409	2,161	2,301,958
Limestone for fertilizer manufacture	165	2,891,835	211	3,605,978
Total	XX	58,763,299	XX	55,897,899

XX Not applicable.
[1]U.S. Customs declared value.

Source: Bureau of the Census.

WORLD REVIEW

Calcium metal was produced in Canada, France, Japan, and the U.S.S.R., in addition to the United States. Market economy country production was estimated to be about 1,500 tons. Total world production was an estimated 2,000 tons. Calcium chloride is a byproduct of synthetic soda ash production, especially in Eastern and Western Europe, and in many cases it is treated as a waste product. The calcium chloride brine from many facilities is dumped into rivers and estuaries. This practice, because of increased pressure from government agencies and environmental interest groups, may be severely curtailed in the future, which could result in a significant increase in the quantity of calcium chloride available in the world marketplace.

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